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A Two-Step Hydrothermal Synthesis Approach to Monodispersed Colloidal Carbon Spheres

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Abstract This work reports a newly developed two-step hydrothermal method for the synthesis of monodispersed colloidal carbon spheres (CCS) under mild conditions. Using this approach, monodispersed CCS with diameters ranging from 160 to 400 nm were synthesized with a standard deviation around 8%. The monomer concentration ranging from 0.1 to 0.4 M is in favor of generation of narrower size distribution of CCS. The particle characteristics (e.g., shape, size, and distribution) and chemical stability were then characterized by using various techniques, including scanning electron microscopy (SEM), FT-IR spectrum analysis, and thermalgravity analysis (TGA). The possible nucleation and growth mechanism of colloidal carbon spheres were also discussed. The findings would be useful for the synthesis of more monodispersed nanoparticles and for the functional assembly.

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Introduction

Carbon-based material is one kind of the most important functional materials because of its unique electromagnetic, thermodynamical, and mechanical properties [1–3] that exhibit potential applications in many areas such as drug delivery, hydrogen storage, junction device, and sensors. Many attempts have been made in the synthesis of nanoparticles with shape control. Spherical nanoparticles are very commonly generated due to the minimum surface energy compared to other morphologies (e.g., films, tubes). Recently, carbon colloidal spheres (CCS) have become an interesting research object for many investigators owing to their potential applications, including high-density and high-strength carbon artifacts lithium storing materials [4–8], sacrificial template to fabricate hollow structures [9–16], catalyst support material in methanol electro-oxidation [17], and coating material in core/shell structure [7, 18, 19]. In addition, these carbon nanoparticles are also potential as building block materials for fabricating ordered close-packed arrays by self-assembly [10, 20], which is also an important research area in nanoscience.

The functional properties of nanoparticles are heavily dependent on their shapes, sizes, and size distribution. Various methods have been used to prepare carbon spheres, such as chemical vapor deposition [21], templating method [22], pyrolysis of carbon sources [23], and hydrothermal method. Among them, the hydrothermal method is widely used due to its advantages, such as high purity, controllable shape and size, and inexpensive operation [24]. Moreover,

the CCS produced by the hydrothermal approach have a hydrophilic surface covered with C–OH groups , which are available for further surface functional modification, as well as the CCS can be easily removed by oxidation at high temperature or by dissolving via enzyme in solution. Therefore, many studies focused on the synthesis of carbon colloids via the hydrothermal approach. For example, Wang et al. [1] were the first to report the hydrothermal synthesis of hard carbon spheres by using sugar as a precursor through heat treatment at 190 °C for 5 h. Li et al. [22] reported that the carbon spheres could be prepared with different sizes from 200 to 1,500 nm under different reaction times (2–10 h, at 160 °C). Later, Mi et al. [25] demonstrated a high-temperature method to produce carbon microspheres with size of 1–2 μm by heating at 500 °C for 12 h in a sealed autoclave. Despite some successes, limitations still exist in generating monodispersed CCS. This is because it is difficult to control or adjust the concentration of the precursor in a sealed system, which will affect the nucleation and growth, and hence the morphology and size of CCS. Therefore, to develop a simple and efficient method to prepare monodispersed CCS is still challenging.

In this work, we report for the first time the synthesis of monodispersed CCS by a two-step hydrothermal approach under mild conditions. A separated nucleation and growth process will be controlled in the proposed method. The particle characteristics (shape, size, distribution) are then characterized by using various techniques, including scanning electron microscopy (SEM), FT-IR spectrum analysis, and thermalgravity analysis (TGA). The possible growth mechanism of CCS prepared by the two-step synthesis approach is also discussed.

Experimental Works

Synthesis of Carbon Colloids

This step aims to synthesize colloidal carbon particles that can serve as seeds in a two-step synthesis approach. In brief, 11.89 g glucose monohydrate (purchased from Tianjin Bodi Chemical Ind. Co. Ltd) was dissolved in 600 mL deionized water, followed by stirring and ultrasonication to insure the solution is homogeneous. The colorless solution was then transferred into a Teflon stainless steel autoclave with 1,000 mL capacity and then sealed closely. Subsequently, the sealed autoclave was heated to 180 °C for 4 h along with constant stirring at ~800 rpm, and then cooled to room temperature naturally. Finally, the suspension containing the as-prepared carbon colloids was transferred into a flask for further characterization and uses. It was found that the particle suspension shows different colors such as deep brown, puce, depending on the particle size.

Synthesis of Monodispersed CCS Particles

The synthesis strategy for the synthesis of monodispersed CCS is similar as those for fabricating polymer and/or silica spherical colloids with narrow size distributions [26–30]. In a typical procedure, the carbon seeds (~93 nm in diameter, Fig. 1f) prepared by one-step approach under the glucose concentration of 0.1 M were divided equally into four parts. Each part was then transferred into an autoclave separately by fixing the total volume at 600 mL, followed by addition of an appropriate amount of glucose with concentrations of 0.1, 0.2, 0.3, and 0.4 M, respectively. The mixture was further heated at 160 °C for 8 h with gentle stirring to insure the reaction homogeneous. After the heating treatment, the reaction system was cooled to room temperature naturally. The precipitates were collected by centrifugation and then rinsed with deionized water and alcohol for three times, respectively. Ultrasonic operation was used to re-disperse the precipitates during the rinsing process. Finally, the colloidal carbon spheres were isolated for further characterizations.

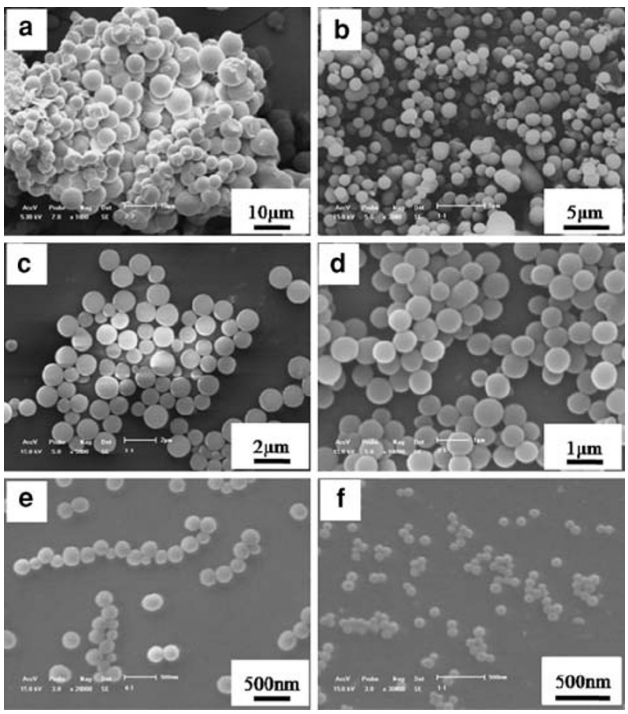

Fig. 1 SEM images of colloidal carbon spheres produced by the one-step approach by heating at 180 °C for 4 h under various concentrations: **a** 1.5 M, **b** 1.0 M, **c** 0.6 M, **d** 0.4 M, **e** 0.2 M, and **f** 0.1 M

Characterization

The morphology and size of the carbon colloidal particles were checked using scanning electron microscope (SHIMADZU, SSX-550, SUPERSCAN Scanning Electron Microscope). To prepare the SEM sample, a drop of the diluted suspension was placed on a glass slide and then it was coated with gold prior to examination. The average particle size was estimated based on the SEM image. FT-IR spectrum (Perkin Elmer, Spectrum one NTS) was used to identify the functional groups. Thermo-gravimetric analysis (HENVEN HCT-2 TG/DTA) was carried out in air for identification of particle stability.

Results and Discussion

One-step Approach for Carbon Colloids

One-step approach was used in this work to prepare carbon colloids that can serve as seeds for monodispersed CCS. Different experimental parameters were tested and optimized. Fig. 1 shows the morphologies of the seeds produced under different concentrations of glucose monohydrate. At higher concentrations (e.g., 0.6, 1.0, and 1.5 M), the colloids are apt to aggregate and show a broad size distribution (diameters of 1–10 μm, Fig. 1a–c). When the concentration of glucose monomers decreases to 0.4 and 0.2 M, the size of particles reduces to ~300 nm (Fig. 1d) and ~220 nm (Fig. 1e), respectively. When the concentration was fixed at 0.1 M, the average diameter of the generated spheres is ~93 nm (see Fig. 1f), with a size distribution of standard deviation of ~11%. This suggested that one-step hydrothermal method could be used to prepare carbon colloids, but the size distribution is still wide, particularly for functional self-assembly.

The influence of reaction temperature on the formation of carbon colloids was also tested in this work. It was found that the suitable temperature range is 160–180 °C (Fig. 1), consistent with the literature [18, 31, 32]. When a low temperature (<140 °C) was used, it is hard to obtain carbon colloids even through a long reaction time (e.g., 24 h); while a high temperature (e.g., over 180 °C) was used, it led to the accelerated nucleation of glucose molecules and resulted in a burst nucleation with a steep decline of the monomer concentration, which would lead to the formation of multiple shapes and/or sizes in the product due to the durative polycondensation [33].

Two-Step Approach for Monodispersed CCS

To achieve monodispersed CCS, the carbon colloids obtained by the one-step approach served as seeds. The size distribution of the seeds is important for obtaining narrow-size particles. Figure 2 shows the SEM images and size distributions that the monodispersed CCS could be prepared by the proposed two-step hydrothermal approach. The size of CCS particle increases with the concentration of glucose (0.1–0.4 M). They are estimated to be 167, 171, 182 and 202 nm in diameters corresponding to the different glucose concentrations of 0.1, 0.2, 0.3, and 0.4 M, respectively. The relationship between the CCS size and the concentration of glucose was fitted and shown in Fig. 3. The standard deviation of particle sizes was calculated to be 8.5, 7.7, 5.4, and 6.9% for the four samples, respectively. This might be achieved by a "self-sharpening growth" process [34–36]. Moreover, no smaller colloids than the seeds (~93 nm in diameter) were generated, confirmed by the SEM images (Fig. 2), indicating that no secondary nucleation occurred by the monomers themselves in the two-step process.

In the optimization of experimental parameters, the concentration of the seeds added in second step can affect

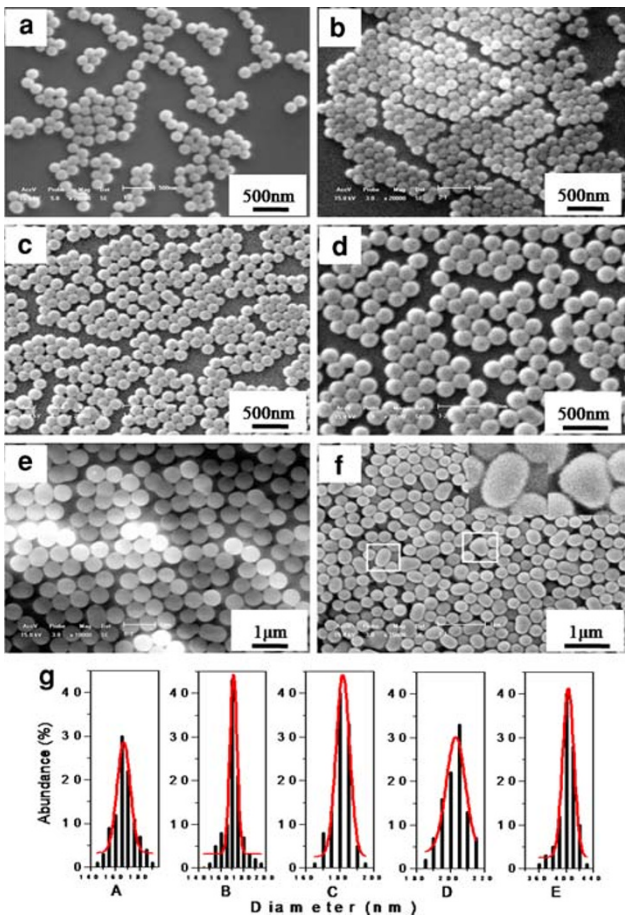

Fig. 2 SEM images of the colloidal carbon spheres synthesized by the two-step approach: **a** 167 nm, **b** 171 nm, **c** 183 nm, **d** 202 nm, **e** 400 nm in diameter, **f** Elliptic and triquetrous particles, and **g** size distributions of CCS corresponding to (**a**–**e**)

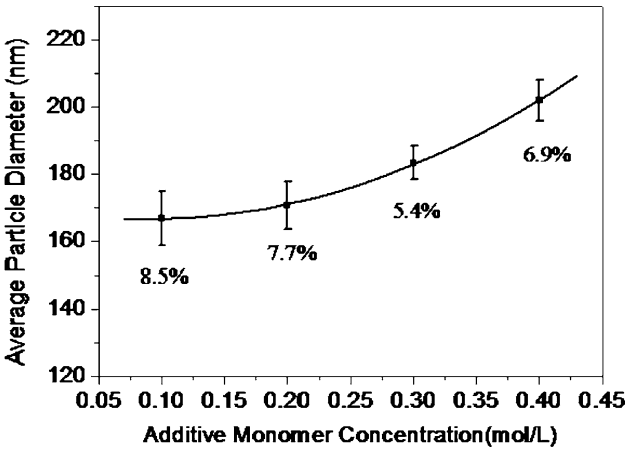

Fig. 3 The *curve* showing the relationship between the concentration of monomers and the CCS particle size. *Error bar* indicates the standard deviation of the particle diameters

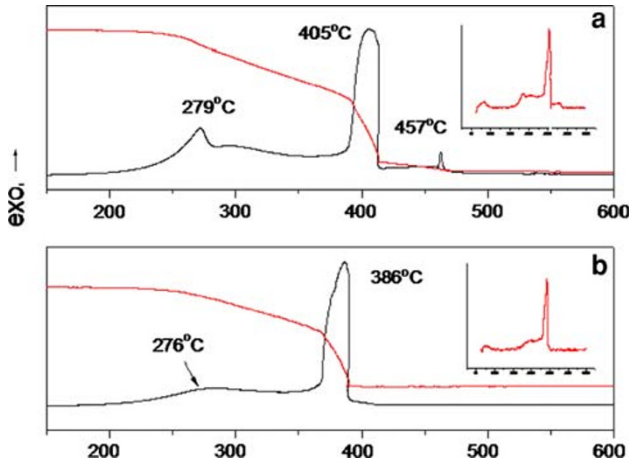

Fig. 4 TG-DTA curves of the CCS synthesized by different processes: **a** two-step approach and **b** one-step approach

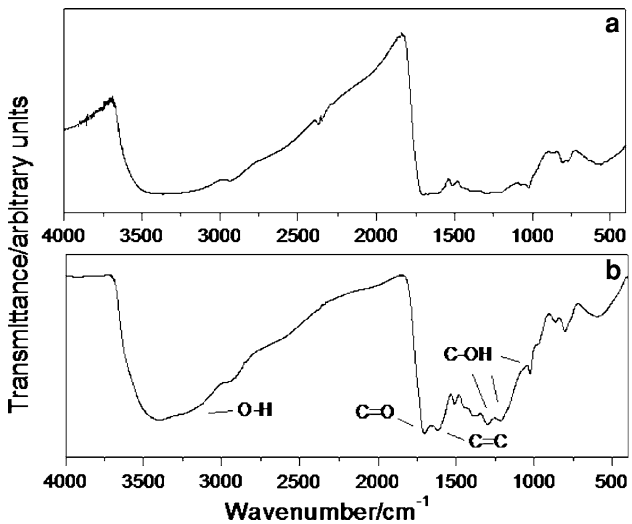

Fig. 5 FT-IR spectrum of the CCS prepared by different processes: **a** one-step approach and **b** two-step approach

the morphologies/sizes of the final product. For example, when 600 mL seed suspension was fully used for the second-step nucleation and growth, the carbon particles obtained show diverse morphologies (elliptic and triquetrous) as shown in Fig. 2f; while one quarter of 600 mL (i.e., 150 mL) seed suspension or less was used, the monodispersed CCS could be preferentially generated (Fig. 2). In addition, various carbon sources were also investigated, including sucrose, starch, and glucose. Sucrose is a kind of disaccharide that decomposes to glucose and fructose easily, which could result in the formation of multi-size colloids. Starch was dissolved into hot water to produce gelatin, non-spherical particles formed in further hydrothermal treatment. Through careful comparison, the glucose is found to be preferential for the synthesis of monodispersed CCS under the reported conditions.

To further understand, the thermal behaviors of the CCS obtained through the above-mentioned two approaches were investigated by using TG/DTA analysis. For those CCS particles obtained by the two-step synthesis process, three exothermic peaks appeared in the curve and centered at around 279, 405, and 457 °C, respectively, as shown in Fig. 4a. The mass loss in the temperature range of 230–390 °C could be attributed to the dehydration and densification of the CCS particles. On the contrary, for those CCS particles obtained by the one-step approach, a remarkable difference in the DTG curve (Fig. 4b) is that no peak was observed at 457 °C. This could be attributed to different combustion processes [10, 31]. This may be caused by different nucleation and growth processes: in the case of one-step process, the glucose monomer can nucleate and subsequently grow without interruption, while for the two-step one, a carbonaceous "core-shell" structure could be formed by polycondensation of the newly added glucose monomers onto the colloidal seed surface. The two separate reaction processes probably result in the difference in density in the "core" (CCS seed) and the "shell" (newly polymerized molecules). The difference may cause two different combustion stages. However, the nature of the difference in thermal behaviors is still not clear. Therefore, more work needs to be performed for better understanding.

As a further confirmation, FT-IR spectrum (Fig. 5) was used to identify the functional groups of the colloidal carbon spheres. The O–H stretching (3,400–3,450 cm^{-1}) and C–OH stretching vibration (1,020–1,380 cm^{-1}) were observed in both samples (Fig. 5a, b). The broad intensive bands imply the existence of a large number of residual hydroxyl groups and intermolecular H-bonds [18, 31].

In addition, two peaks located at 1,704 and 1,617 cm^{-1} could be assigned to C=O vibration and in-plane C=C stretching vibration of aromatic ring [18], respectively, observed from those particles generated by the two-step process (Fig. 5b). On the contrary, these two peaks are too weak to distinguish clearly for those carbon particles prepared by one-step process (Fig. 5a), probably caused by an incomplete aromatization.

Formation Mechanism

The mechanism governing nucleation and growth of the CCS in the two-step approach was discussed. Different growth mechanisms were proposed in the past. For example, Wang et al. [4–8] suggested that the formation of dewatering sugar spherules is similar to the emulsion polymerization procedure. At a certain temperature, the dehydration and polycondensation leads to the appearance of amphiphilic compound, and the formation of spherical micelles that can further nucleate by dewatering. Li et al. [18, 37] described the effect of critical supersaturation of glucose monomers and observed a nucleation burst when some macromolecules formed by intermolecular dehydration of linear or branchlike oligosaccharides. Recently, Yao et al. [31, 32] reported the transformation of fructose to 5-hydroxymethylfurfural through an intra-molecular dehydration process followed by subsequent formation of carbon spheres. Such a carbon sphere contains a dense hydrophobic core and a hydrophilic shell. Such differences in understanding particle nucleation and growth drive us to conduct such work.

In this case, the polymerization of glucose monomers is built up by intermolecular dehydration, which is critical to nucleation in the hydrothermal synthesis. It is supposed that in the homogeneous solution, the polymerization reaches supersaturation, and then nucleation occurs with the progress of dehydration and aromatization. In the proposed two-step synthesis approach, the active functional groups on the surface of the carbon colloids could react preferentially with the newly added monomers to form bigger particles instead of nucleation by the monomers themselves. This was also confirmed by the following theoretical explanation.

In principle, colloidal growth in a supersaturated solution usually proceeds in two modes: diffusion-controlled mode and reaction-controlled mode [38, 39]. Under different conditions, either the diffusion process or the reaction process becomes the rate-determining step of the overall growth process. Generally, the slower one would dominate the overall growth of the particles. For the diffusion-controlled mode, the particle growth rate (dr/dt) is described by

$$\frac{dr}{dt} = \frac{DV_m}{r}\left(1 + \frac{r}{\delta}\right)(C_b - C_e) \quad (1)$$

where D is the diffusion coefficient of the solute, V_m is the molar volume of solute, r is the particle radium, δ is the thickness of the diffusion layer, C_b is the bulk concentration of monomers, and C_e is the solubility of the particle as a function of its radius. If $r/\delta \ll 1$, Eq. 1 can be rewritten as

$$\frac{dr}{dt} = \frac{DV_m}{r}(C_b - C_e) \quad (2)$$

where the growth rate via diffusion-controlled mode is inversely proportional to the particle radius, consistent with the theory of Ostwald ripening [40]. Our experimental observations (Fig. 2) are in good agreement with the Eq. 2.

For the reaction-controlled mode, particle growth rate is given by [38, 39]

$$\frac{dr}{dt} = K_i V_m (C_b - C_r) \quad (3)$$

where K_i is the surface integration constant. Eq. 3 indicates that the growth rate of colloidal particles is independent of the particle size. If taking Gibbs–Thomson effect into account, Eq. 1 can be expressed as

$$\frac{dr}{dt} = \frac{2\gamma DV_m^2 C_\infty}{rRT}\left(\frac{1}{r^*} - \frac{1}{r}\right) \quad (4)$$

where r^* is the particle radius in equilibrium with the bulk solution, C_∞ is the solubility of the solid with infinite dimensions, γ is the specific surface energy, R is the gas constant, and T is the absolute temperature. Equation 2 is then expressed as:

$$\frac{d(\Delta r)}{dt} = \frac{2\gamma DV_m^2 C_\infty R\Delta r}{RT\tilde{r}^2}\left(\frac{2}{\tilde{r}} - \frac{1}{r^*}\right) \quad (5)$$

where Δr is the standard deviation of the particle size distribution and $\tilde{r}$ is the mean particle radius. Equation 5 reveals that the change rate of standard deviation ($d(\Delta r)/dt$) depends strongly on the particle radius (r^*) in equilibrium (supersaturation) in the diffusion-controlled mode. Higher supersaturation ($\tilde{r}/r^* < 2$) below the critical supersaturation makes better monodispersity ($d(\Delta r)/dt < 0$). Otherwise, lower supersaturation ($\tilde{r}/r^* \geq 2$) can broaden the size distribution ($d(\Delta r)/dt > 0$) even in the diffusion-controlled mode [38, 39]. In the proposed two-step approach, the standard deviation was reduced from 8.5% down to 6.9% with increasing the monomer concentration from 0.1 to 0.4 M (Fig. 3) indicating that a higher monomer concentration that determines the supersaturation is favorable for the narrow size distribution under the considerable conditions. On the basis of above-mentioned analysis, the diffusion-controlled mode may be dominant in the overall growth of particles in our proposed two-step synthesis method, which is apt to the formation of monodispersed particles.

Conclusion

We have demonstrated a facile two-step hydrothermal approach to the synthesis of monodispersed CCS under mild conditions. By this approach, the CCS size could be controlled in the range of 160–400 nm with a standard deviation 6–9%. Compared to the one-step approach, the proposed two-step approach could separately control the nucleation and growth of particles as far as possible, which is favorable for the narrow size distribution. It was noted that in the concentration range of 0.1–0.4 M, the higher the concentration of monomers the narrower the size distribution of carbon colloids. The nucleation and growth of the CCS might be attributed to the diffusion-controlled mode. This method could be extended into other systems for the fabrication of monodispersed particles with functional properties.

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